Montana PEM Membrane Degradation Study, Year 1 Report

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Objectives

- Develop a system capable of measuring current and voltage performance for each membrane in a proton exchange membrane (PEM) fuel cell stack and record the performance of each individual cell.
- Develop a single-cell PEM fuel cell to allow in situ synchrotron X-ray measurements of the cell in operation.
- Perform initial magnetic resonance microimaging experiments on membrane materials.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Distributed Generation Systems

- E. Durability
- G. Power Electronics

Components

- P. Durability

Approach

- Design a system to capture individual cell performance in real time (current, voltage, temperature points taken every 0.5 milliseconds).
- Test the stack response as it is subjected to load transients. Monitor each cell in the stack for its entire lifetime.
- As failures occur, analyze the cell using X-ray techniques, including methods that provide spatial resolution and chemical composition information.
- As failures occur, analyze the membrane material using magnetic resonance imaging (MRI) microimaging techniques to get information about membrane permeability.
- Search electrical records of failed membranes to see if mode of failure or an electrical signature of failure can be discerned.

Accomplishments

- A fuel cell monitoring system has been constructed and undergone initial testing.
- An individual synchrotron-compatible fuel cell has been constructed and tested at the National Synchrotron Light Source (NSLS).
- Initial MRI microimages of membranes have been obtained.

Future Directions

- Modify the fuel cell monitoring system; then, run and monitor fuel cells under transient load change conditions.
- Perform further X-ray analysis of membrane electrode assemblies (MEAs) on new cells to get baseline information before degradation occurs.
- Start construction of an electrophoretic MRI probe so mobility in membranes under field testing can be measured.
- Perform X-ray work on any degraded membranes.
- Perform MRI work on any degraded membranes.

Introduction

The Montana State University PEM Membrane Degradation project is geared towards determining how and why membranes in fuel cells degrade and fail. By monitoring every individual membrane in a fuel cell 2000 times/sec while the cell is subjected to real-world use, we hope to: 1) cause the types of degradation users typically see, but in a controlled environment; 2) determine an electrical signature that will identify what causes failure, or at least warns of impending failure; 3) perform advanced X-ray and MRI characterization of the degraded membranes to provide information that may result in improvements of the membrane material; and 4) perhaps allow design of electronic control systems that will prevent fuel cells from operating under conditions where damage is likely to occur.

Approach

The Montana State University PEM Membrane Degradation project has three interdependent components: 1) Fuel Cell Electrical Characteristics Monitoring, 2) Synchrotron Based X-Ray Characterization of Membranes, and 3) Nuclear Magnetic Resonance (NMR) Microscopy of Polymer Electrolyte Membranes. The project will involve continuous, comprehensive monitoring of PEM fuel cell electrical performance while the cell is being

subjected to real-world types of loads and transients. A fuel cell enclosure will contain 80 membranes housed in 8 cartridges. Each side of the cartridge (5 membranes) will contain an analog-to-digital (A/D) converter that will measure voltage for each individual membrane, current and temperature at a 2000 Hz rate. This total of 224,000 data points per second will be stored to provide a permanent record of performance of each individual membrane over its entire life span. This comprehensive set of data has promise of yielding an electrical signature of impending failure. Membranes in various states of degradation and failure will be extracted for characterization using the two analytical techniques in the project.

X-ray characterization will be used to investigate the catalyst and possible poisoning of the catalyst, via X-ray Photoelectron Spectroscopy. In addition, a synchrotron-compatible fuel cell has been constructed to perform measurements during operation. If the electrical monitoring program identifies load conditions that generate degradation, in situ measurements can be performed under these conditions to determine chemical changes in the catalyst, and possibly in the membrane material itself. These measurements can be performed with 10 mm or better spatial resolution so localized effects and spreading of damage can be studied, which may provide insight into the mechanism of failures. NMR

microimaging techniques will also be utilized to investigate membrane performance. Rather than imaging the membrane itself, this technique will provide images that contain information about water and hydronium ion mobility within the membranes. These imaging experiments will be performed on membranes in various states of degradation.

Results

Fuel Cell Electrical Characteristics Monitoring. We have designed, built, and tested three prototypes of a USB serial interface, 14-bit, 280,000 sample/sec analog-to-digital converter board. This unit features an AD7856 converter, a 50 MIPS Ubicom SX28 controller, and a DLP design USB interface module. The timebase stability is 50 ppm. The measured noise variance is typically less than 1.5 LSB, or about .009 percent of full-scale. In addition to superior signal performance, our custom solution is better than commercial alternatives because its small size allows us to locate the analog-to-digital conversion physically closer to the fuel cell cartridges. Most data collection alternatives would require us to route hundreds of wires carrying sensitive analog measurements in close proximity. This would lead to cross-talk and noise pickup between the leads that would likely degrade the measurements far beyond the inherent capabilities of commercial products.

The data acquisition module is useful for other research at CTA. In addition, the Massachusetts Institute of Technology (MIT) and Woods Hole Oceanographic Institute (WHOI) have expressed considerable interest in the hardware. Both groups are interested in the novel capabilities and small size of our design relative to commercial offerings. MIT student Jim Paris is presently rewriting the Linux kernel driver for the USB interface and working with Greg Linus Torvalds and Kroah-Hartman (creators of Linux, and the Linux USB drivers, respectively) to ensure that the MSU/MIT enhancements are incorporated in future releases of Linux. WHOI is interested in using the board for next-generation instrument packs that are affixed to marine animals, where small size and low power are obvious concerns.

We are presently designing an analog instrumentation-grade front end that goes between the

USB data acquisition board and the fuel cell cartridges. We've identified a wiring scheme for each fuel cell cartridge, where voltage and temperature measurements are carried from the cartridge to the analog board via CAT5e twisted pairs. The fuel cell modules plug into the front-end instrumentation using modular connectors so that the modules are easy to swap out when the membranes fail. A key part of the front-end instrumentation is a new Analog Devices high-common mode range amplifier with integrated, trimmed, precision front end resistors. This unit features common mode rejection exceeding the rails, which is needed to isolate individual membrane potentials from the stack. The Analog Devices unit also comes with an auxiliary amplifier to adjust the voltage output range to that of the A/D converter. The cost of this instrumentation from Tektronix, for example, would exceed $100,000 for the number of channels we are considering.

The storage server is at the highest level of the data acquisition hierarchy. We have assembled an SMP (simultaneous multi-processing) AMD Athlon based machine with two 1.4 Terabyte RAID-5 hot-swap arrays. These have a combined capacity of 2.8 Terabytes. In addition to disk hot-swap capability, the server has a redundant hot-swapable power supply system. All fans and other moving parts are also hot-swap. We project that this will be sufficient for approximately the first year of measurements with appropriate compression.

A major contribution of the project is that we will expose membranes to realistic transient load conditions. Creating these conditions requires a transient capable DC active load. We've purchased a set of these from Agilent and are presently testing them. We have also designed and built our own active load. Testing for this device has been postponed in the interest of proceeding to the measurement stage as quickly as possible.

Synchrotron Based X-Ray Characterization of Membranes. For this fiscal year, the following accomplishments were made. A graduate student (Alex Lussier) and a Research Experience for Undergraduates (REU) participant built a synchrotron-compatible fuel cell for in-situ X-ray characterization of the catalytic materials of the fuel cell during operation to identify performance degradation

mechanisms. Chemical state and local structure information by X-ray absorption spectroscopy (XAS) and by X-ray absorption fine structure (XAFS) will identify the environment of the catalytic materials. These results will be compared to X-ray characterization of fuel cell components that have shown performance degradation to identify the failure mechanism. We will be able to identify catalytic poisoning and map out the poisoning element with good spatial resolution (a few microns resolution).

From the support of this program, MSU is now a Participating Member in two beamlines at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory. The first is the soft X-ray MSU Nanoscale Materials X-ray Characterization Facility at U4B (Spokesperson Y.U. Idzerda), and the second is a hard X-ray Absorption Fine Structure beamline at X23B (spokesperson Bruce Ravel). Both are open facilities for any research programs, but we now have guaranteed access.

For preliminary work, we are characterizing the small fuel cell power output as a function of the hydrogen gas flow, air flow, and the load. We can compare these measurements to the performance curves for a commercial fuel cell measured elsewhere at MSU. This commercial cell is not compatible with the synchrotron techniques, although disassembly of the fuel cell and characterization of the catalytic and membrane materials will be a part of this research project.

In addition to the in-situ X-ray characterization, we have initiated a project of modeling diffusion in fuel cells to identify failure modes. Finite element modeling of hydrogen ion and heat diffusion in PEM fuel cells has identified a possible mechanism for thermal failure of the membrane due to membrane thickness variations. This modeling will also assist us in understanding the performance degradation due to diffusion barriers at interfacial regions (from structural modifications or alloying) and due to catalytic poisoning.

NMR Microscopy of Polymer Electrolyte Membranes. To date, we have focused on obtaining PEM samples, establishing the wet lab experimental protocol for sample preparations following prior NMR work[1] and establishing the NMR microscopy

methods for imaging of PEMs. Before investigation of the PEM membrane, polymer hydrogel samples were used to establish the NMR methods. Figure 1 shows NMR microscopy data for a 500 μm thick sample of hydrogel material. The hydrogel is cut into a 5 mm diameter disk and placed into a 6 mm diameter 500 μm thick Teflon (PTFE) sample holder with supernatant distilled H_2O. The images are of calculated NMR parameters-T_1 relaxation (Figure 1a), T_2 relaxation (Figure 1b) and translational diffusion coefficient (Figure 1c)-and have an in-plane spatial resolution of 78 μm/pixel. The NMR signal is being obtained from the (^1H) protons on the water molecules within and external to the hydrogel. Spin-lattice, or T_1, relaxation depends on the mechanisms available for energy transfer between the spins and thermal energy repositories such as translations, vibrations and rotations of the lattice. In a polymer gel matrix (or a polymer membrane such as a PEM), the presence of paramagnetic impurities or electron rich elements such as oxygen are a source of relaxation which depends on the chemistry of the matrix. The physical structure of the matrix-for example, the extent of cross linking in a gel-also impacts the relaxation by affecting the molecular motion of the water within the matrix and the resulting fluctuation rate of the magnetic fields. Hence, both the matrix mobility and chemical composition impact the T_1 relaxation behavior in the sample. The T_1 value for the water in the hydrogel, shown in light blue in Figure 1a, is measured to be 2 s, while that of the free water, shown in purple in Figure 1a, is 2.2 s. This indicates enhanced relaxation rate $1/T_1$ of the water within the gel due to the restricted motion of the water molecules.

Spin-spin, or T_2, relaxation is due to interactions between the nuclear magnetic moments of the sample. The relaxation is due to the fluctuations in magnetic field from the dipole interactions due to molecular mobility [2, 3]. T_2 values in solids are very short, indicating the fast magnetic relaxation rate, $1/T_2$, due to strong coupling of the dipole moments. In liquids, T_2 is much longer since the motion of the spin generates motional averaging of the relaxation mechanism that results in a slow relaxation rate. The T_2 of the water within the hydrogel, shown in light blue in Figure 1b, is 122 ms, while that of the free water surrounding the sample, shown in purple, is 165 ms. The restricted mobility
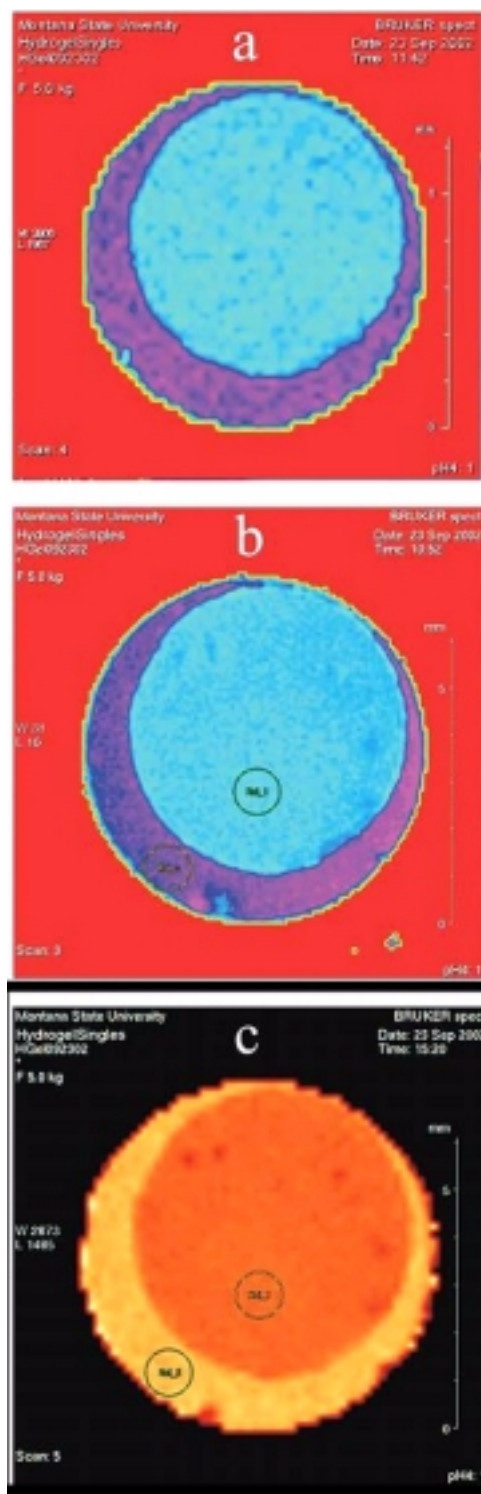
Figure 2. a) MRI microimages of the T_1 weighted water concentration within a 178 µm thick disk of Dupont Nafion 117. The image intensity is proportional to water concentration weighted by T_1 relaxation so that the free water surrounding the disk appears as black. Thus, the black regions within the disk indicate regions where water mobility is similar to free water. b) MRI map of the spatial T_2 distribution within the sample.

Figure 1. MRI microimages of a) T_1 relaxation, b) T_2 relaxation and c) diffusion coefficient of the water constrained within the matrix of a polymer hydrogel. The images are a top view of a 5 mm disk (light blue in a0 and b0) in a 6 mm diameter sample cell.
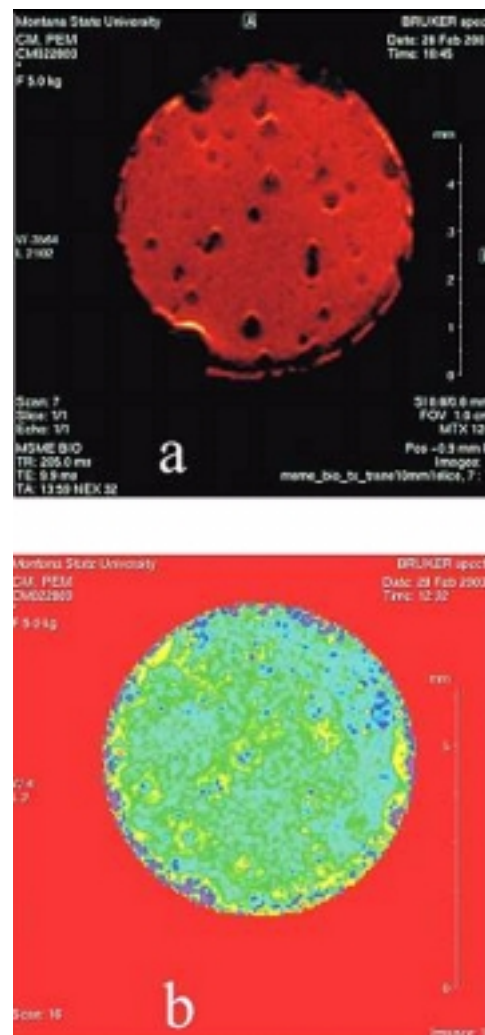
within the hydrogel reduces the motional averaging of the spin-spin interactions, resulting in enhanced relaxation rate $1/T_2$. Consistent with the spatially resolved T_1 and T_2 data is the molecular translational self-diffusion coefficient of the water shown in Figure 1c. The orange region shows the slower self-diffusion of the water within the hydrogel, 1.95×10^{-9} m^2/s, relative to the free water of brighter yellow with a diffusion coefficient of 2.45×10^{-9} m^2/s.

These values of self-diffusion coefficient are in excellent agreement with those found from bulk NMR measurements without spatial resolution [4].

Preliminary images of Dupont Nafion117 PEMs have been acquired. While *bulk* NMR measurements of electroosmotic mobility [1] and molecular self-diffusion of water [5] within PEMs have been reported, to our knowledge the images in Figure 2 are the first *spatially* resolved *images* of water within a PEM. The sample cell and in-plane spatial resolutions are the same as those used in Figure 1, 78 mm/pixel, with the data averaged over the 178 μm sample thickness. The image in Figure 2a is of the water concentration within the PEM weighted by the T_1 relaxation behavior, in contrast to the calculated T_1 value maps in Figure 1a where the intensity of the image is directly the calculated T_1 value. The T_1 weighting is such that the signal from free water is completely relaxed and gives no signal. Figure 2b is a T_2 map of the PEM, with red indicating small T_2 values with increasing T_2 through yellow, green, blue and purple. Comparison of Figure 2b and Figure 1b indicates the significant heterogeneity of the magnetic relaxation behavior within the PEM. The holes in Figure 2a could be the result of either highly mobile water or water in contact with strong chemical relaxation centers. Interpretation of these images will require significant experimental and theoretical analysis, including combining NMR measurements of T_1, T_2 and time dependent self-diffusion, and is ongoing.

Conclusions

The three-pronged approach shows promise for yielding insights to degradation mechanisms and the changes in materials properties that result.

FY 2003 Publications/Presentations

1. Joseph D. Seymour, Sarah L. Codd, James C. Mabry, Scott C. Busse and Eric S. Peterson. "NMR microscopy of water and methanol distribution and dynamics in polymer electrolyte membranes." North American Membrane Society, 14th Annual Meeting, Jackson Hole, WY, May 17-21, 2003.

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2. E. Fukushima and S.B.W. Roeder, *Experimental Pulse NMR: A nuts and bolts approach*, Reading, MA: Addison-Wesley, 1981.

3. P.T. Callaghan, *Principles of Nuclear Magnetic Resonance Microscopy*, New York: Oxford University Press, 1991.

4. P. McConville and J.M. Pope, A comparison of water binding and mobility in contact lens hydrogels from NMR measurements of the water self-diffusion coefficient. *Polymer*. **41**: 9081 (2000).

5. S. Hietala, S.L. Maunu, and F. Sundholm, Sorption and diffusion of methanol and water in PVDF-g-PSSA and Nafion 117 polymer electrolyte membranes. *Journal of Polymer Science: Part B: Polymer Physics*. **38**: 3277 (2000).